The Eni - IFP/Axens GTL Technology: From R&D to a Successful Scale-U*p*

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Abstract

Proven natural gas reserves had reached about 184 Tscm in 2006 to which 36% is stranded gas far from the final market. Fischer Tropsch based GtL options today represent a viable route to develop such remote gas resources into high quality fuels and specialties. Thus opening different markets for the gas historically linked to the oil.

Thanks to R&D successful improvements in the field of catalysis and reactor technology coupled with optimized integration and economies of scale have reduced the investment cost for building a Fischer Tropsch GtL complex. Basically all major Oil & Gas companies are involved in proprietary GtL development, and today several industrial projects have been announced. The most advanced is the Oryx project (QP-Sasol) which has been inaugurated the 6th of June '06 and currently in the starting up phase.

Eni and IFP-Axens have developed a proprietary GtL Fischer-Tropsch and Upgrading technology in a close collaboration between the two groups.

The Eni/IFP-Axens technology is based on proprietary catalysts and reactor, designed according to scale-up criteria defined in ten years of R&D activity.

Unique large scale hydrodynamic facilities (bubble columns, loops) bench-scale dedicated pilot units, as well as large scale Fischer-Tropsch pilot plant, have been developed and operated to minimize reactor and ancillaries scale-up risks.

The large scale Fischer-Tropsch pilot plant has been built and operated since 2001. The plant, located within the Eni refinery of Sannazzaro de' Burgondi (Pavia, Italy) is fully integrated to the refinery utilities and network. It reproduces at 20 bpd scale the overall Fischer Tropsch synthesis section: from slurry handling (loading, make-up, withdrawal), to reactor configuration and products separation units. Today the scale-up basis has been completed and the technology is ready for industrial deployment.

Introduction

World natural gas consumption has grown steadily since the seventies, and today accounts for 23% share of the world energy demand. The *International Energy Agency* is expecting natural gas to become the second energy source, ahead of coal, thanks to its affirmation in power generation. Drivers to this change are the increase in the known reserves of natural gas, the need to monetize stranded gas reserves and the environmental pressure to minimize the flaring of associated gas.

The estimated amount of natural gas reserves has been continuously increasing, moving from the 1994 estimation of 146 Tscm to over 184 Tscm in 2006 [1]. The total amount of *Stranded Gas Reserves* has been estimated to be 66.5 Tscm, 36% of the gas proven reserves (average of published data).

All these factors play a role in the new strategic relevance of the gas-to-market technologies to transport the gas from the production area to the final market.

In the last 20 years thanks to the technological evolution in this area the market for the natural gas has changed its nature from regional to international, so that today it is possible to foresee a globalization of the gas and derivatives markets, similarly to the oil one.

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Different technologies are today available to bring the gas on the market covering long distance: high pressure/capacity pipelines, liquefaction and regassification of natural gas (LNG), electric power generation and wire transportation (Gas-to-Wire), and finally natural gas conversion into liquid hydrocarbons, the so called *Gas-to-Liquids* (GtL). GtL is the process of natural gas conversion into transportable liquids, characterized by an intermediate step of natural gas conversion for producing synthesis gas. Today there are two main technologies: the production of oxygenate liquid compounds (methanol and dimethylether - DME) and the Fischer-Tropsch synthesis for production of high quality middle distillates (i.e. jet, kero and diesel fuel), base-oil, or waxes.
The final market for LNG pipeline and wire transportation is the traditional natural gas one, while for GtL technologies the final products destination is the automotive fuel market, the chemical market or the use as fuel for electricity production (figure 1).
In the last decades the technical, social and economical scenario is favouring the GtL tendency to produce synthetic fuels via Fischer-Tropsch.

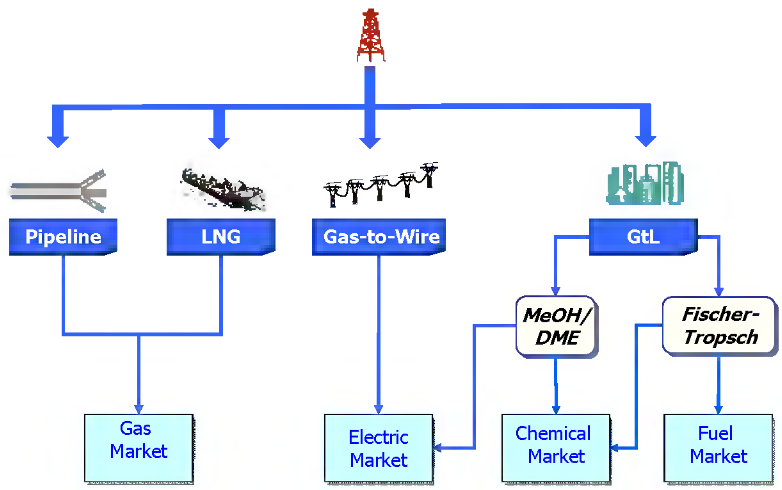

Figure 1. *Gas to Market* options

The Fischer-Tropsch Process

In recent years, interest has increased significantly in using Fischer-Tropsch-based processes. Discovered at the Kaiser Wilhelm Institute (Germany) in 1923 by Franz Fischer and Hans Tropsch, the process has never seen a real commercial development. In the past, only particular geopolitical situations favoured the realization of industrial plant for fuels and chemicals production, starting from coal. It was the case of various German companies during World War II and for Sasol in South Africa during the period of the embargo.
Current Fischer-Tropsch GTL technology consists of three major sections (figure 2) centred on *low temperature Fischer-Tropsch synthesis*. Syngas generation and product upgrading technologies have extensive commercial experience; nevertheless their application to Fischer-Tropsch process needs an intensive integration activity to obtain the most cost-effective combination of these three technologies. Moreover the "new" low temperature Fischer-Tropsch approach has been limited to pilot, demo or small-scale commercial units (Shell – Bintulu)

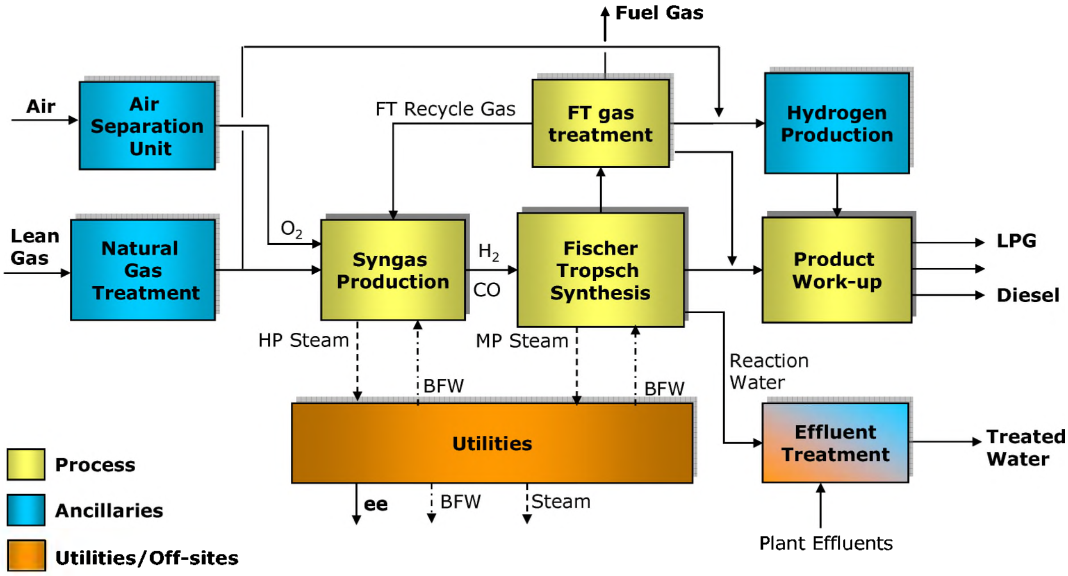

Figure 2. FT-GtL complex scheme

The low temperature Fischer-Tropsch synthesis is based on the R&D advancement for both catalyst and reactor technology. Catalyst and reactor selection influence the various characteristics of the Fischer Tropsch process such as the thermal efficiency, heat removal, product selectivity and operating costs.

Several types of catalysts can be used for Fischer-Tropsch synthesis. The most common ones are based on iron (Fe) or cobalt (Co). Generally iron-based catalysts are cheaper and produce gasoline, hydrocarbons, and linear alpha olefins, as well as a generally unwanted mixture of oxygenates such as alcohols, aldehydes, and ketones. Iron catalysts have considerable water gas shift activity, and therefore produce excessive amounts of carbon dioxide. Nevertheless, the water gas shift activity can be advantageous when the syngas contains a low H_2/CO ratio.

The results obtained with cobalt catalyst, compared with the historical iron based technology, allow high yields in long chain linear paraffins that can be efficiently transformed into valuable products (middle distillates) by means of hydroprocessing steps.

Fischer-Tropsch synthesis reactions are highly exothermic, and the reactor systems must have provisions for removing this heat. Two are the major types of reactors today considered for modern - low temperature - GtL applications: multi-tubular fixed bed (FBR), slurry bubble column (SBCR). Heat removal, pressure drops control, catalyst handling and reactor capacity represent the most critical factors which inevitably affects the process economics. To this regard the two reactor solutions deeply differ in the control of such critical items. In a SBC reactor, catalyst particles (20-200 μm) are suspended in a slurry medium formed by the product, liquid at reaction condition (20-30 bar, 200-240 °C), and the syngas fed into the bottom of the column. Such conditions enable an optimum control of the heat and material exchange rate on the catalyst surface as well as reactor capacities around 17.000 bpd.

The efficiency of the gas-liquid-solid mixing and the solid-liquid separation represent some of the technical challenges successfully won by the R&D.

Fischer-Tropsch GTL Product Markets

Due to the impossibility to produce finished products directly from the Fischer-Tropsch reaction the key factor is the production of high molecular weight paraffins, namely wax, to be hydroprocessed into lighter products such as middle distillates. Among the different FT-GtL products, the diesel fraction, in particular, is highly valued in the downstream market because of its excellent properties that meet environmental regulations aimed at a reduction emissions standard for light- and heavy-duty diesel vehicles. The FT-GtL fuel reduces emissions relative to conventional diesel, as it contains near-zero sulphur and aromatics (table 3). A GtL complex with an optimized design for middle distillates production can reach 75% diesel + kero yield.

Table 3. Conventional vs. GTL Diesel quality

Quality	Conventional Diesel	FT - Diesel
Boiling range (°C)	150-360	150-360
Density @ 15°C (kg/m^3)	820 – 845	780
Sulphur (ppm vol)	50 – 10	< 1
Aromatics (% vol)	30	< 0.1
Cetane number (CN)	> 51	> 70
CFPP* (°C)	- 15	- 20
Cloud point (°C)	-8§	-15

* Cold Filter Plug Point; § Winter diesel

Fischer-Tropsch GTL Project Development

In the last decades several companies have been involved in intensive R&D program to develop their own GtL technology with different technological solution (table 1).
Currently there are only two commercial natural gas-based Fischer-Tropsch GtL plants. In 1992 PetroSA started up the world's first major commercial plant at Mossel Bay in South Africa. That plant used three Sasol's Synthol circulating fluidized-bed reactors to produce liquid transportation fuels (about 22,500 bpd) at high temperature and gas phase. PetroSA is today in joint venture with Statoil for the development of a GtL technology for natural gas conversion, based on a modern SBCR and cobalt catalyst technology.
In 1993, Shell started up a 12,500 bpd Fischer-Tropsch GtL plant at Bintulu in Malaysia for production of diesel fuel and other specialty products including lube base stock and solvents. The unit is based on the Shell Middle Distillates Synthesis process (SMDS) which use a fixed bed reactor, operated at low temperature, and cobalt catalyst.

Table 1. Fischer Tropsch technologies

Company	Syngas	Fischer-Tropsch	Upgrading
BP	BP/Davy Compact Reformer	BP fixed-bed process. Co catalyst.	-
ConocoPhillips	Catalytic Partial Oxidation (CoPox)	Slurry phase process. Co catalyst	-
Eni/IFP	-	Eni/IFP slurry phase process. Co catalyst.	Axens HDK process. Eni/IFP catalyst.
ExxonMobil	ExxonMobil fluidized combined reforming §	ExxonMobil AGC-21 slurry phase process. Co catalyst.	ExxonMobil
Rentech	-	Slurry phase process. Fe catalyst.	-
Sasol	-	Sasol Slurry Phase Process (SSPD). Co catalyst.	Chevron
Shell	Shell Partial Oxidation	Shell Middle Distillates Synthesis (SMDS). Fixed-bed process. Co catalyst.	Shell
Statoil	-	Slurry Phase Process. Co catalyst	-
Syntroleum	Syntroleum Air Blown Autothermal Reforming	Slurry Phase Process. Co catalyst.	-

§: ATR (Topsoe - HTAS) technology for Qatar project

Sasol has by far the most commercial experience with Fischer-Tropsch coal-based synthetic fuels production which is based on iron catalyst and low capacity Arge reactor or two phases

(G/S) high temperature Synthol reactors. Today Sasol, in joint venture with Chevron, is proposing its new slurry phase Fischer-Tropsch process (SSPD) based on cobalt catalyst and developed at pilot scale (figure 3).

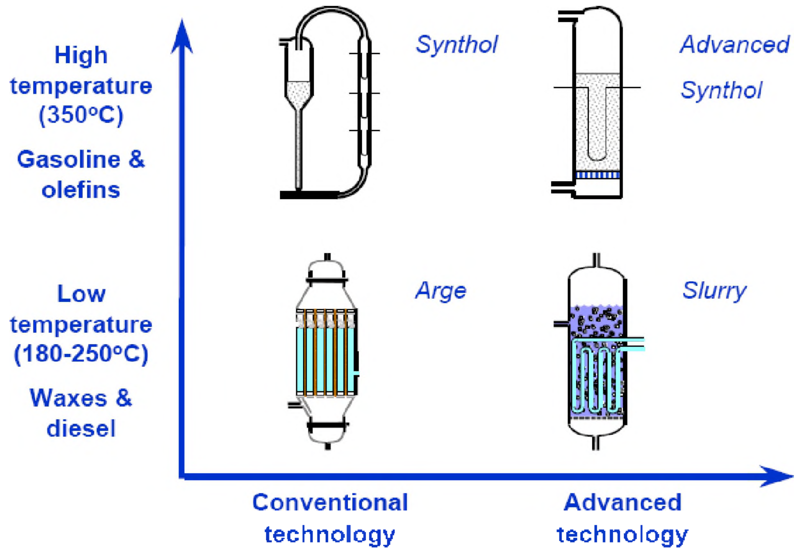

Figure 3. Sasol's reactor technology

Other companies involved in GtL development are BP, ConocoPhillips, Eni, IFP, ExxonMobil, Rentech, and Syntroleum.
For the next ten-year there are worldwide at least nine commercial GtL projects, at various stages of planning and development, initiated by companies operating in gas-rich countries such as Qatar, Iran, Russia, Nigeria, Australia, and Algeria, where natural gas can be developed at a cost of less than one USD per million Btu. Six GtL projects are located in the state of Qatar as joint ventures based on an integrated development and production sharing agreement (DPSA) with major international oil companies (table 2). Qatar has established a favourable climate in terms of transparent business, investment policies and stable tax regulations. In addition Qatar has invested substantially to develop infrastructure and services to support development of its natural gas resources.

Fischer-Tropsch Process Economics

The economics of GtL continue to improve with advances in technology, economies of scales, optimal utilities integration within the complex by efficient utilisation of internal energy.
Capital costs have dropped significantly, from more than 100,000 USD/bpd (USD per barrel of total installed capacity) for the original plants to a range of about 50,000 $/bpd (KBR's EPC contract is valued at USD1.7 billion) [2] in the case of NPC/Chevron project in Nigeria and 30,000 USD/bpd [3] for the Oryx project phase one where local conditions are optimal and the EPC contract have been sign in a period ('03) of favourable economic circumstances.
Operating costs are estimated at 4-5 USD/bbl, a part from the costs of feedstock and transportation.
GtL project profitability analysis is strongly dependent on the cost of gas and the price for upgrading products, which is tied to the price of crude oil. In a medium-low investment cost environment (35,000 USD/bpd), the internal rate of return is fairly above 15% for crude oil prices scenarios (Brent) around 30 USD/bbl and gas price of 0.5 USD/Mbtu (pre taxes, 25 years project life).

Table 2. GTL Commercial Projects

Owner	Syngas technology	FT technology	Capacity, Kbpd	Status	Start-up date
Qatar Petroleum (51%), Sasol (49%) Oryx GtL project - Qatar	HTAS ATR	Sasol SBCR	Two phases: 34 + 66	06/06/06 Plant inauguration Under start-up phase	3rd Q 2006, expansion in 2009
NNPC (25%), Chevron (75%) Escravos GTL Project (EGTL) - Nigeria	HTAS ATR	Sasol SBCR	34	FEED completed in 2004 by Foster Wheeler. EPC phase. Contractor JSK: consortium (JGC, KBR, Snamprogetti)	2009
Shell Pearl GtL Project - Qatar	Shell POX	Shell Fixed bed reactor	Two phases: 70 + 70	FEED completed. EPC awarded to KBR/JGC, EPC phase launched 27/07/06	2009, expansion in 2011
Qatar Petroleum SasolChevron	HTAS ATR	Sasol SBCR	130	Evaluation phase. Project Delayed	-
Marathon Oil	Syntroleum Air-blown ATR	Syntroleum SBCR	120	Pre-FEED work completed end 2003. Project Delayed.	-
ConocoPhillips	C-POX	SBCR	Two phases: 80 + 80	Statement of Intents (SOI) with QP signed in Dec. 2003. Pre-FEED initiated. Project Delayed.	-
ExxonMobil	HTAS ATR	Exxon SBCR	150	Head Of Agreement (HOA) with QP signed in July 2004.	2011

The Eni – IFP/Axens GtL process development

Eni has developed a proprietary Fischer-Tropsch and Upgrading technology jointly with the Institut Français du Petrole (IFP) and its process & licensing branch Axens in a technological collaboration which started at the beginning of '96.
The GtL Eni/IFP-Axens technology has been designed according to strategy based on three main targets:

1. Development of an innovative FT/HDK technology based on tailored catalysts, proprietary FT reactor design and an optimized product upgrading steps (hydrocraking).
2. Engineering studies of fully integrated GTL complex, today case by case, at BPD and pre-FEED level.
3. Minimization of scale-up risk by developing the *right tools* for scale-up.

Both the catalysts and the technology have been developed and optimised thanks to several dedicated facilities available and still in operation at licensors sites.
Unique large scale hydrodynamic facilities (mock-up bubble columns, loops) have been developed and operated to make reactor and ancillaries scale-up easy and mostly risk less Hydrodynamics, as well as mass and heat transfer, thermodynamics and kinetics have been described in a detailed reactor model, validated up to 2500 bpd equivalent size. The reactor model is integrated in process simulator commercial software: such a tool reproduces the whole plant equipment and provides material and heat balances (figure 4).
A large scale Fischer-Tropsch pilot plant has been built and operated since 2001. The plant is located inside the Eni refinery of Sannazzaro de' Burgondi (PV, Italy) and is completely linked to refinery utilities. It reproduces at a smaller scale (20 bpd) the overall FT synthesis

section: from slurry handling (loading, make-up, withdrawal), to reactor configuration (internal gas recycle), to products separation units. Due to the proper size of the plant, it was possible to assess a wide range of industrial operating conditions in order to select those that optimise catalyst performances. During the several runs carried out, different types of liquid-solid separation devices have been assessed and the best working one (as efficiency and long term reliability) has been adopted for the industrial complex.
An important operating experience has been achieved and operating instructions consolidated for the industrial unit. DCS platform of the pilot pant can be used as a dynamic training simulator, to reproduce critical operations, off-sets, emergencies, etc.
The large scale FT pilot plant is still in operation and is considered a valuable tool for trouble shooting on different parts of the technology (figure 5).

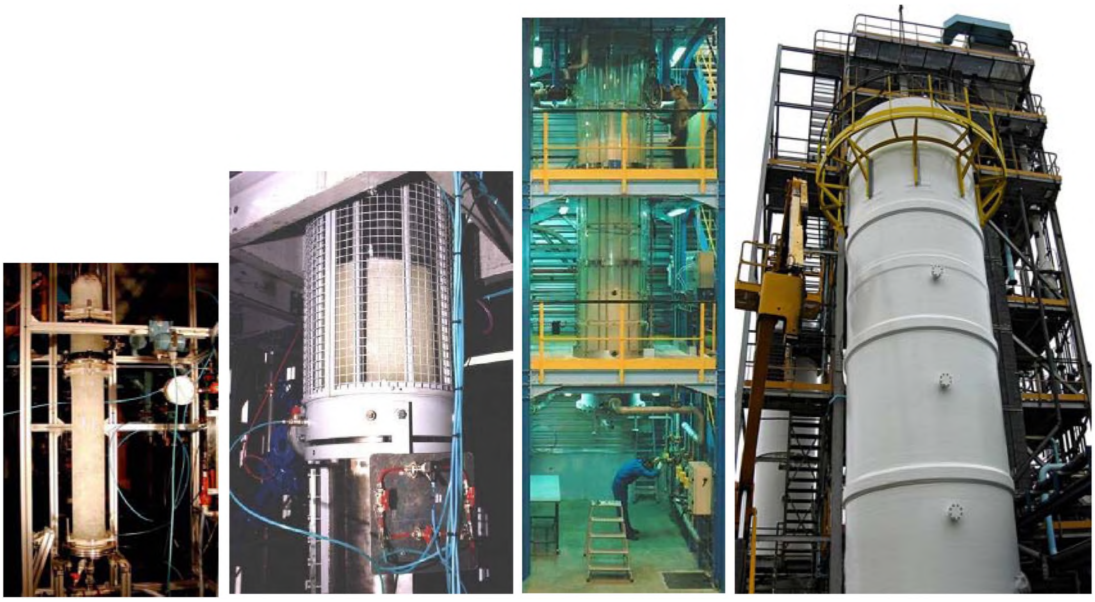

Figure 4. Eni/IFP hydrodynamic facilities, Lyon (France)

Figure 5. Eni/IFP FT pilot plant, Sannazzaro (Pavia, Italy)

In addition to pilot plant facility, special laboratory equipment for FT catalyst scale-up has been designed in order to reproduce, under reaction conditions, the mechanical attrition expected in the commercial size reactor. This task has been achieved only thanks to the knowledge developed in the slurry bubble columns hydrodynamics field, given from extensive experimental data set to most sophisticated Computer Fluid Dynamics skills.
Today the scale-up bases have been completed and the technology is ready for industrial deployment.

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